AD/A-002 195

HYDROGEN PEROXIDE TANK SAFETY

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Naval Research Laboratory

Prepared for:

Coast Guard

November 1974

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

| REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|---|---|---|
| 1. REPORT NUMBER<br>NRL Memorandum Report 2921 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER<br>HD/A-002 195 |
| 4. TITLE *(and Subtitle)*<br><br>HYDROGEN PEROXIDE TANK SAFETY | | 5. TYPE OF REPORT & PERIOD COVERED<br>Final Report |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(*s*)<br><br>Robert N. Hazlett, Jack P. Stone and<br>James M. Hall | | 8. CONTRACT OR GRANT NUMBER(*s*)<br><br>Z-70099-4-42580 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br><br>Naval Research Laboratory<br>Washington, D. C. 20375 | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS<br><br>DOT-USCG-Z-70099-4-<br>42580;42580<br>NRL Prob. C01-01.601 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>U. S. Coast Guard<br>Office of Research and Development<br>Washington, D. C. 20375 | | 12. REPORT DATE<br>November 1974 |
| | | 13. NUMBER OF PAGES<br>49 |
| 14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)* | | 15. SECURITY CLASS. *(of this report)*<br><br>UNCLASSIFIED |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Hydrogen Peroxide
Fire Exposure
Chemicals Shipping Hazards

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The U. S. Coast Guard has the responsibility for regulating
water transport of chemicals in U. S. ports and inland    ters.
In support of that responsibility, NRL has evaluated t    effect
of a vigorous fire on a 4,000 gallon aluminum transport container
for hydrogen peroxide. Heat transfer calculations show that
the bare tank would fail in about five minutes in a fire
(Abstract continues)

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20. (Continued Abstract)

exposure but that one-inch insulation would protect the tank and contents for at least 30 minutes. Additional calculations, combined with experimental $H_2O_2$ decomposition rates, predict that the critical self-heat temperature for one-inch insulation, while lower than that for the bare tank, would be acceptable.

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# HYDROGEN PEROXIDE TANK SAFETY

Robert N. Hazlett, Jack P. Stone and James M. Hall

## INTRODUCTION

Hazardous chemicals are an important article of commerce and large quantities are being shipped by water and overland. Recent accidents with some of these materials (1,2) stimulated further examination of the hazards associated with the transport of oxidizers, corrosive chemicals and pressurized and liquified gases. The United States Coast Guard has the responsibility for regulating water transport of such chemicals in U. S. ports and inland waters. In the present instance, they are concerned with the hazards associated with proposed containers (See Appendix I) for transporting 4,000 gallons of 70 percent hydrogen peroxide, particularly the behavior of such a container and its contents in a severe fire when on the deck of a ship. This report describes work supported by the U.S. Coast Guard Office of Research and Development at NRL to address this hazard.

The proposed $H_2O_2$ tanks in which the foreign product will be shipped will be constructed from 99.5% aluminum. The Coast Guard does not normally allow the use of aluminum for tank construction because of its poor high temperature strength. In this case, however, aluminum is necessary to minimize the decomposition rate of the cargo. The calculations in this work are engineering estimates made to study the effect of a vigorous fire on a nominal 4,000 gallon bare aluminum container of 70% hydrogen peroxide. In addition, the effect of two different insulation thicknesses on heat transfer from a fire to the tank was estimated. We also experimentally determined the rate of decomposition of a stabilized 70%

hydrogen peroxide over the temperature range 122-275°F (50-135°C), the latter temperature being 18°F (10°C) above the normal boiling point. The experimental decomposition rate was utilized to calculate gas venting requirements for the 4,000 gallon tank and the heat liberated by $H_2O_2$ decomposition at different temperatures. The latter results were used along with heat transfer rates from bare and insulated tanks in a post-fire regime to estimate self-heat temperatures for the $H_2O_2$ container.

## DECOMPOSITION RATES

The readiness with which hydrogen peroxide may be decomposed into water and molecular oxygen is a characteristic which has been familiar since the discovery of this substance. It is a property both useful and troublesome and one brought about in many ways. Rates of decomposition vary over an extremely broad range from the exceedingly low values obtainable with carefully purified material under optimum conditions to the very rapid decomposition required in the use of concentrated peroxide as a rocket propellant. Controlling factors include temperature, pH, catalysis and radiation. Typical catalysts are heavy and transition metals such as silver, copper, iron, chromium and mercury (3). Catalysts may be either homogeneous or heterogeneous.

The importance of concentration of hydrogen peroxide solutions in relation to the hazards of decomposition is shown by the fact that above 65 weight percent the heat liberated is sufficient to vaporize all the water present plus that formed by decomposition (4). The adiabatic decomposition temperature of 90 percent peroxide is 1380°F (750°C). Normally in storage the heat liberated is dissipated to the surroundings with a temperature rise of 1°C or less.

All hydrogen peroxide solutions decompose during storage. Decomposition is minimized (5) by: (a) the initial production of hydrogen peroxide in a state of high purity, (b) the addition of certain substances, called stabilizers, which counteract the effect of catalytic impurities or container surfaces, and (c) control of the environment to which the hydrogen peroxide is exposed. Cleanliness in all handling procedures is essential.

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Stabilizers include sodium stannate, sodium pyrophosphate and 8-hydroxyquinoline (6,7). The nature of container surfaces is critical to peroxide stability. Suitable materials include pure aluminum, pure tin and Pyrex glass. In addition to container wall characteristics, surface/volume ratio is significant.

Pure hydrogen peroxide, in the absence of catalytic contaminants and in a thoroughly clean container of noncatalytic material, is a surprisingly stable substance. Typical data with high quality unstabilized hydrogen peroxide indicate a decomposition rate not in excess of 0.002% per hour for 90% peroxide at 50°C (8). In the presence of a small quantity of stabilizer this value may be reduced to 0.0003% per hour at 50°C (3,8).

Temperature has an exponential effect on the decomposition rate of pure, unstabilized hydrogen peroxide. The effect is defined by the expression (3,9)

$$(T_2 - T_1)\log a = 10 \log(k_2/k_1),$$

where $T_2$ and $T_1$ are temperatures in °C, and $k_2$ is the decomposition rate at $T_2$ and $k_1$ is the rate at $T_1$. The temperature coefficient "a" has been found to have a value of 2.2 ± 0.1 over the range 50° to 90°C (8). This indicates that the rate more than doubles for each 10°C rise in temperature, or increases about fifty-fold for the interval 50° to 100°C. Some typical decomposition data for 90% hydrogen peroxide are given in Table 1 (7,8).

The intent of the present work was to investigate decomposition rates of 70% hydrogen peroxide over a temperature range up to and above the normal boiling point (125°C for 70 wt-%). Previously reported work on hydrogen peroxide stability was done largely with 90% material. Reproducibility of results was a problem at 100°C and above and a lower temperature was commonly employed, for example 50°C. In the present problem decomposition rates of particular significance are those at: (a) the ambient temperatures encountered in transportation and (b) the temperatures resulting from a fire situation, especially the decomposition rate up to the

## TABLE 1

### Stability of 90% Hydrogen Peroxide At Various Temperatures

| Temperature | Approx. Rate of Decomposition |
| --- | --- |
| 30°C (86°F) | 1% per year |
| 66°C (151°F) | 1% per week |
| 100°C (212°F) | 2% in 24 hours |
| 140°C (284°F) | Decomposes rapidly with boiling |

## TABLE 2

### Summary of Tests on Decomposition Rate
### of 70% Hydrogen Peroxide

| Temp., °C | Decomposition Rate, %/day | |
| --- | --- | --- |
| | By $O_2$ Evolution | By Wt. Loss |
| 50 | 0.0144 | 0.012 |
| | 0.0148 | 0.020 |
| 75 | 0.0744 | 0.079 |
| | 0.0747 | 0.082 |
| 95 | 0.454 | 0.413 |
| | 0.400 | 0.400 |
| 110 | 0.99 | --- |
| | 1.02 | 1.00 |
| 125 | 3.75 | 2.90 |
| | 3.96 | 3.93 |
| 135 | 8.13 | --- |
| | 5.70 | --- |

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boiling point at the relief pressure of the 4,000 gallon
container. Pressure is said to have no effect on the
rate (7).

## Experimental

Procedure - The product used in the decomposition
tests was a 70% hydrogen peroxide obtained from a U. S.
company. Analysis gave a concentration of 70.0 weight
percent.

Three methods for the determination of decomposition
rates were employed: measurement of the volume of
oxygen evolved, of the weight loss, and of the change
in peroxide concentration. The first proved the most
satisfactory. The very small weight changes observed
made the second method marginal. The third method was un-
satisfactory due in part to the small concentration
changes experienced. Furthermore, an analytical preci-
sion of not less than 0.01% was required and this was
not obtainable, even with burdensome replicate analyses.
Both the second and third methods are more appropriate
for long-term tests or tests where large changes in
concentration occur.

In this report decomposition rate is defined as a
percent of the peroxide originally present decomposing
in unit time. Thus, rate is a percent of a percentage.
The percent decomposed per hour or day must be distinguish-
ed from the percent concentration change. For example,
starting with 70.0% peroxide a rate of decomposition of
1%/day would indicate a concentration of 69.3% remaining
after 24 hours.

In the oxygen evolution or gasometric method, a
cleaned, noncatalytic vessel containing the peroxide
sample is held at a constant temperature and the oxygen
evolved is collected at constant pressure (1 atm.) in a
gas buret over water. From the volume of oxygen,
allowing for saturation with water vapor and correcting
to standard conditions, the amount of peroxide decomposed
can be calculated. Figure 1, shows the type of apparatus
used for tests below 100°C. The reaction vessel, connect-
ed through capillary tubing to a water-jacketed gas buret

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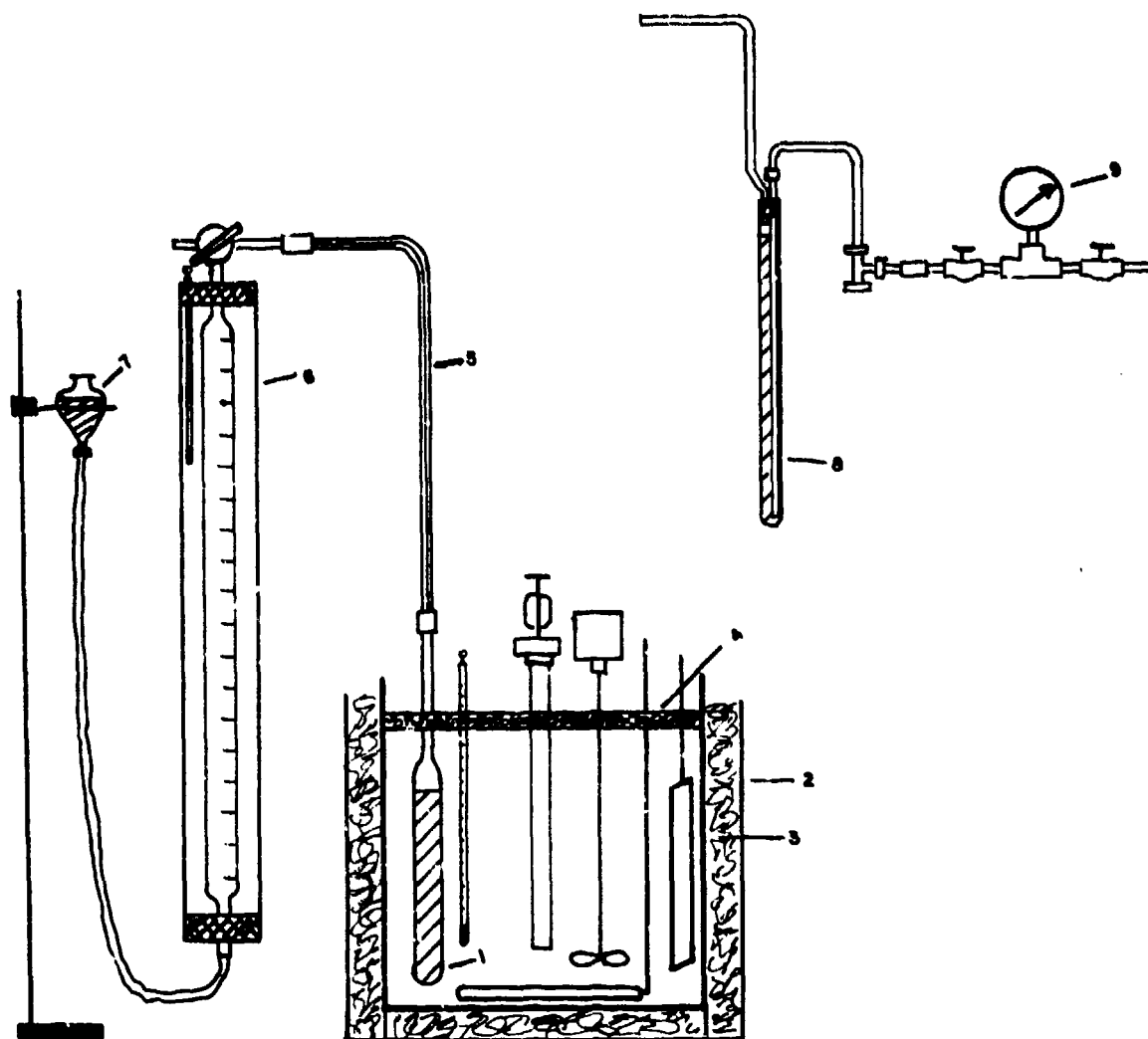
1. REACTION (DECOMPOSITION) TUBE)
2. CONSTANT TEMPERATURE BATH
3. INSULATION
4. SHREDDED POLYFOAM PLASTIC
5. PYREX CAPILLARY TUBING

6. 100 ML GAS BURET WITH
   WATER JACKET
7. WATER LEVELING BULB
8. 25 CM MERCURY MANOSTAT (FOR
   TESTS ABOVE BOILING POINT)
9. PRESSURE GAGE

Fig. 1 – Apparatus for decomposition rates by gas evolution

with leveling bulb, is supported in an insulated
thermostated water bath. Our reaction vessels were
heavy wall Pyrex tubes 9 inches long by 1 inch O.D.
An integral upper tube 8 inches long by 1 cm O.D. extend-
ing above the bath, permitted any escaping water vapor
to condense and flow back. Volume of these tubes was
57 ml. Temperature of the bath was controlled to
approximately 0.2°C. In the tests at 75° and 95°C a
layer of shredded polyfoam plastic effectively retarded
evaporation from the bath. The reaction tubes were
cleaned by standing filled with concentrated nitric
acid for 24 hours or more followed by thorough rinsing
with distilled water. They were then pre-conditioned
by standing with 70% hydrogen peroxide. For the tests
above 100°C, the reaction tube was supported in a well
in an insulated aluminum block furnace. The well was
filled with a silicone oil. Temperature was controlled
to 0.5°C. Temperature of the silicone oil was measured
with thermometers and recorded with a thermocouple. Tests
at 135°C were conducted under a pressure of 5 psig since
135° is above the normal boiling point of 70% hydrogen
peroxide. The pressure was established and controlled
by a 25 cm mercury column interposed between the reaction
tube and the capillary leading to the gas buret. A
pressure gage was connected by means of a polyethylene
tee to permit leak testing and to monitor the reaction
pressure. In the 135°C tests, an air stream directed
at the narrow upper part of the reaction tube cooled it
to prevent loss of any water vapor. This precaution
applied only to the weight loss method of measuring the
decomposition.

Weight of the reaction tube was measured on an
oversized analytical balance accurate to about 0.5 mg.
Weight losses were usually under 100 mg and rates
calculated therefrom had an accuracy of 5 to 10%.
Peroxide concentration was determined by titration of a
small sample or aliquot with standard 0.1 N ceric ammonium
sulfate. Precision of the analysis was 0.2% or better.
However, this equated to a precision of only about ±50%
in the calculated decomposition rate. Thus the titration
method is unsuitable with small changes in concentration
of peroxide.

The time period of measurement ranged from 2 weeks at 50°C to 4 hours at 135°C. In addition to the overall average rates reported in Table 2, the incremental rate was observed to ensure its constancy.

Results - A summary of experimental results is presented in Table 2 and Figure 2. It is apparent that duplicate tests agreed well, with one exception, and that the data from weight loss supported the more accurate results from oxygen evolution very well. The decomposition rate of 0.014%/day at 50°C in Table 2 agrees well with previously published data since it lies between minimum reported values for stabilized and unstabilized hydrogen peroxide (8). It is concluded that the peroxide we used must be stabilized. However, no chemical tests for the presence of stabilizers were made. Figure 2 is a plot of the decomposition rates calculated from oxygen evolution versus temperature. The slope of the graph equals the log of the temperature coefficient "a". We found a value of 2.08 for "a" in this work.

Conclusions - In translating the above results to the 4,000 gal aluminum peroxide tank, several points must be kept in view. First, the data above represent ideal or minimum values for the decomposition. Second, stability of the foreign peroxide is not known. Further, factors such as smoothness and catalytic nature of the container surface, pre-conditioning of the surface, the presence of any dirt or contaminant and the surface/volume ratio can have significant effects on decomposition rates (8,10).

## HEAT TRANSFER ANALYSIS

Since hydrogen peroxide solutions decompose with evolution of heat at ordinary temperatures and at rates which increase with temperature, its storage tank must lose heat at some minimal rate. Otherwise, the tank self-heats. According to Shanley (4), the hazard created by self-heating is due to pressure rise in the tank, the final outcome of which depends primarily on the $H_2O_2$ concentration. For example, adiabatic decomposition of 90 wt % $H_2O_2$ can produce a temperature of 1380°F (750°C),
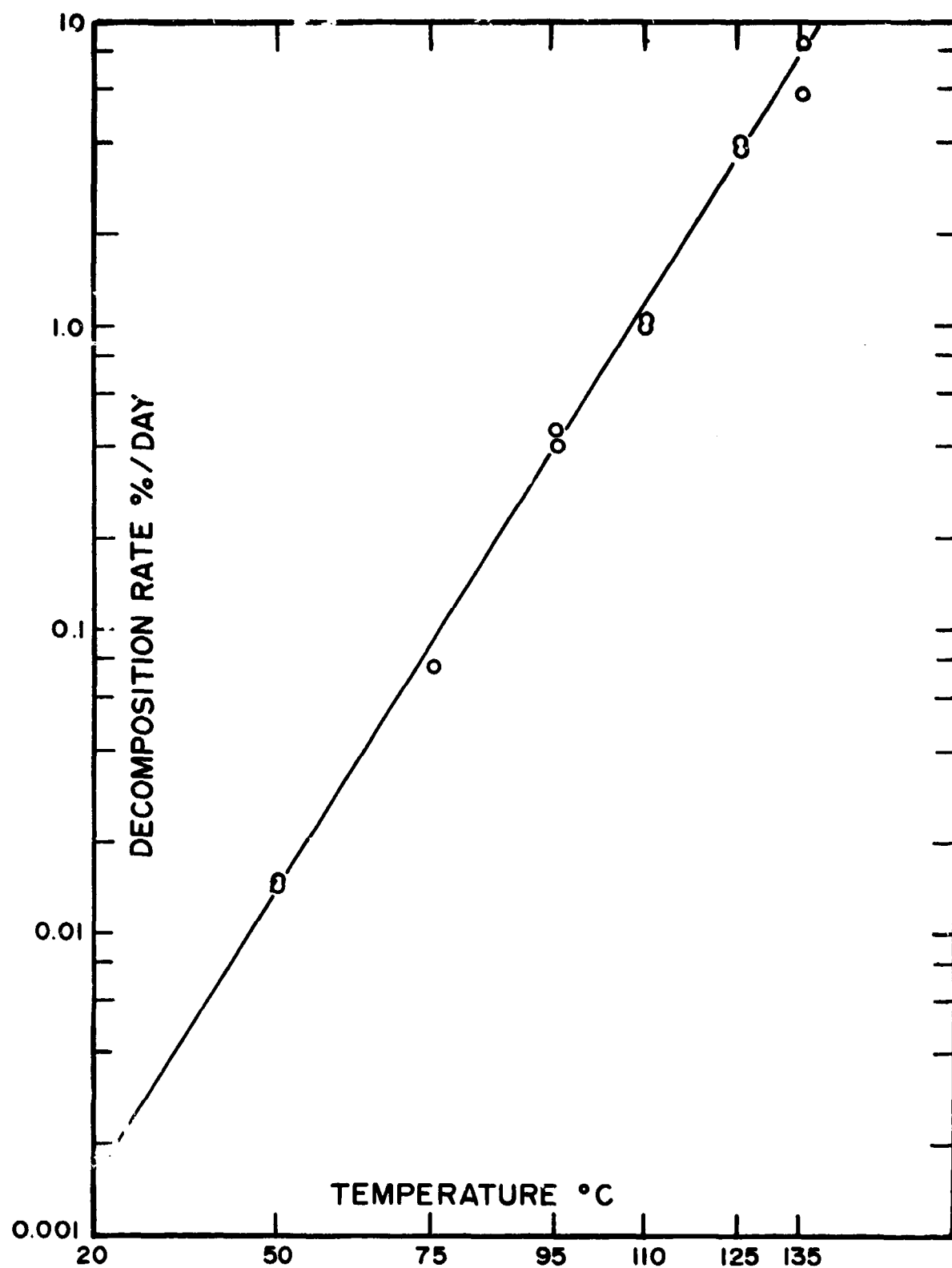
Fig. 2 – The decomposition rates of 70% hydrogen peroxide

while 12 wt % produces 212°F (100°C).  It is important
then that H$_2$O$_2$ tanks lose heat.  In fact, Shanley recom-
mends that storage tanks be bare.

On the other hand, if H$_2$O$_2$ tanks are involved in an
intense, unwanted fire, uninsulated tanks are rapidly
heated and, as this analysis indicates, may fail in less
than 5 minutes.

In this study, we consider conditions of self-heating
and of fire involvement for the 4,000 gallon, 99.5%
aluminum tank containing 70 weight percent H$_2$O$_2$ aqueous
solution, as described by the Eisenbahn-Verkehrsmittel
Aktiengesellschaft (Eva) (11).  Both uninsulated (bare)
and insulated (2.76 inches thick and 1.0 inch thick)
tank conditions are included.  In fire involvement, we
consider a suggested period of 30 minutes.

## Self-Heating Conditions

For usual ambient H$_2$O$_2$ temperatures, a heat balance
for the tank of H$_2$O$_2$ exists so that the heat lost from
the tank equals the heat gained due to decomposition
of the H$_2$O$_2$, and an equilibrium H$_2$O$_2$ temperature is
established.  However, if H$_2$O$_2$ decomposition were to
release more heat than could be dissipated, the H$_2$O$_2$
temperature would rise and create a self-accelerating
decomposition.

In Figure 3, heating and cooling curves are presented
for the three tank conditions:  bare, 2.76-inch (70 mm)
insulation, and 1.0-inch (25 mm) insulation.  A thermal
conductivity of 0.043 BTU/(hr)x(ft)x(°F) was used for
the insulation.  Curves labeled A and B are heating curves
that result from the H$_2$O$_2$ decomposition.  Curve A shows
the heat-release rate calculated for a decomposition rate
of 0.9% per year at 77°F (25°C) (NRL measurement) as the
ordinate versus the average temperature of the H$_2$O$_2$
solution as the abscissa.  Curve B represents a decompo-
sition rate arbitrarily chosen as five times the rate of
curve A since impurities in the H$_2$O$_2$ solution usually
increase the decomposition rate.

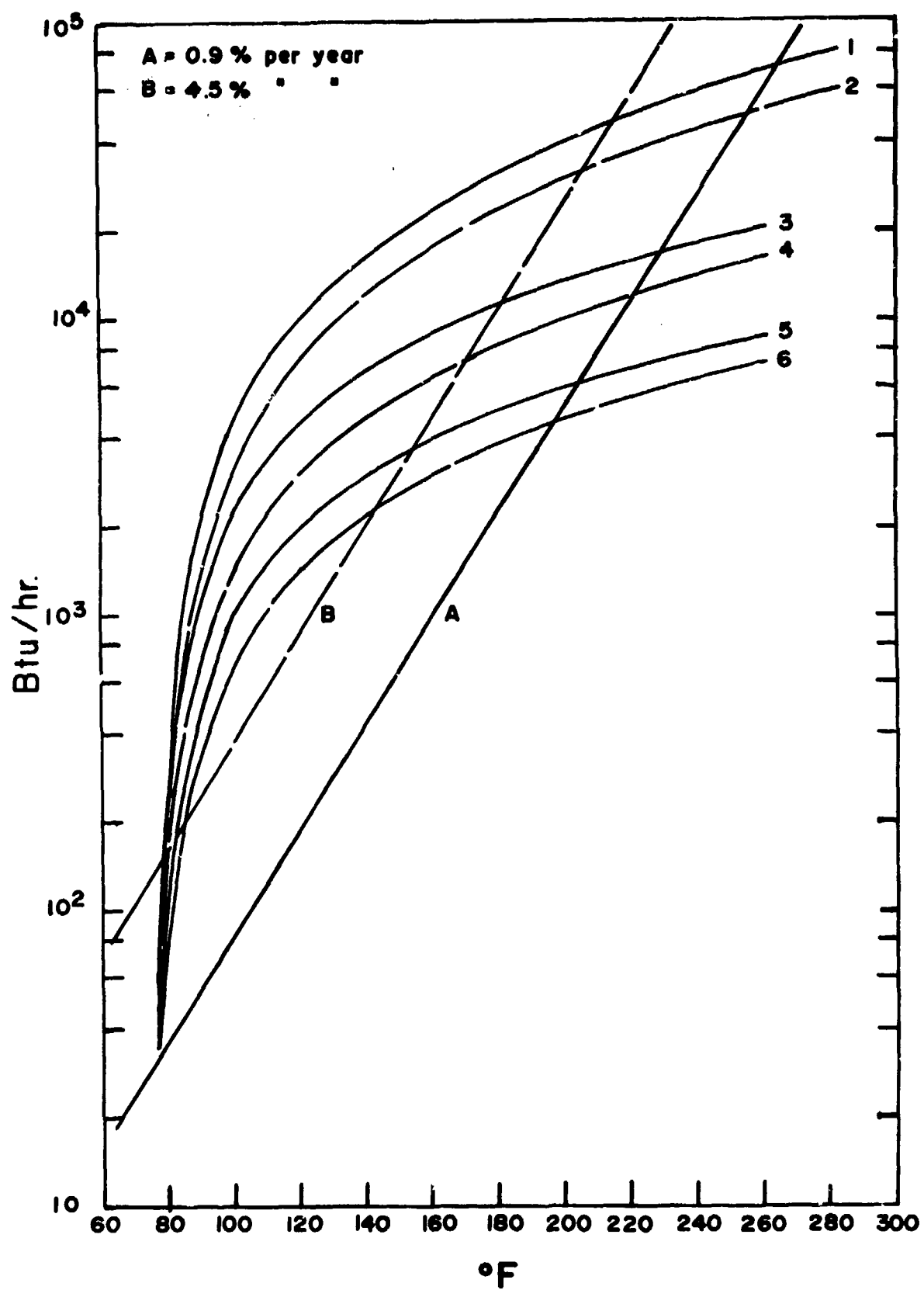The cooling curves shown in Figure 3 are numbered.

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Fig. 3 - Heat balance

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Curves 1 and 2 are estimates of heat lost from the bare tank. For these curves, the ordinate is the rate of heat lost from the tank, and the abscissa is the temperature of the $H_2O_2$ solution. For curve 1, we assume that the tank loses heat by radiation as well as by free convection, whereas for curve 2, heat is lost only by free convection. Curves 3 and 4 show similar assumptions for the heat losses with 1 inch of insulation and curves 5 and 6 with 2.76 inches of insulation. These cooling curves are calculated with the assumption that ambient temperature is 78°F (25.5°C).

Intersections of the heating and cooling curves in Figure 3 at the lower temperatures represent predicted equilibrium temperatures where heat released by decomposition equals heat lost by the tank, while the intersections at the higher temperatures are those predicted for the start of accelerated self-heating. So long as $H_2O_2$ remains below these limiting temperatures, the tank will cool back to equilibrium with its surroundings (78°F for these cooling curves). Appendix I shows dimensions of the tank and calculations for Figure 3 are given in Appendix II, Part I.

### Fire Involvement

If a 4,000 gallon tank containing 70 wt-% $H_2O_2$, as described, is involved in an intense, enveloping fire, what happens during the first 30 minutes? In answer to this question, we attempt to predict ti.. and events as based on available information (12-16) and on calculation. Such hazardous events may occur as: (a) heat of $H_2O_2$ above the limiting temperature, (b) release of $H_2O_2$ into a fire by the tank-pressure-relief system, (c) tank rupture, and (d) explosion of $H_2O_2$ vapor.

Bare Tank - In Figure 4, a graphical summary of predictions is presented for fire involvement for the bare tank; temperature is plotted versus time. It is assumed that the fire begins at time zero ($\theta = 0$) and that heat flux in the fire remains constant in all directions $(q/A = 34,500 \frac{Btu}{(hr) \times (ft)^2})$. Further, it is
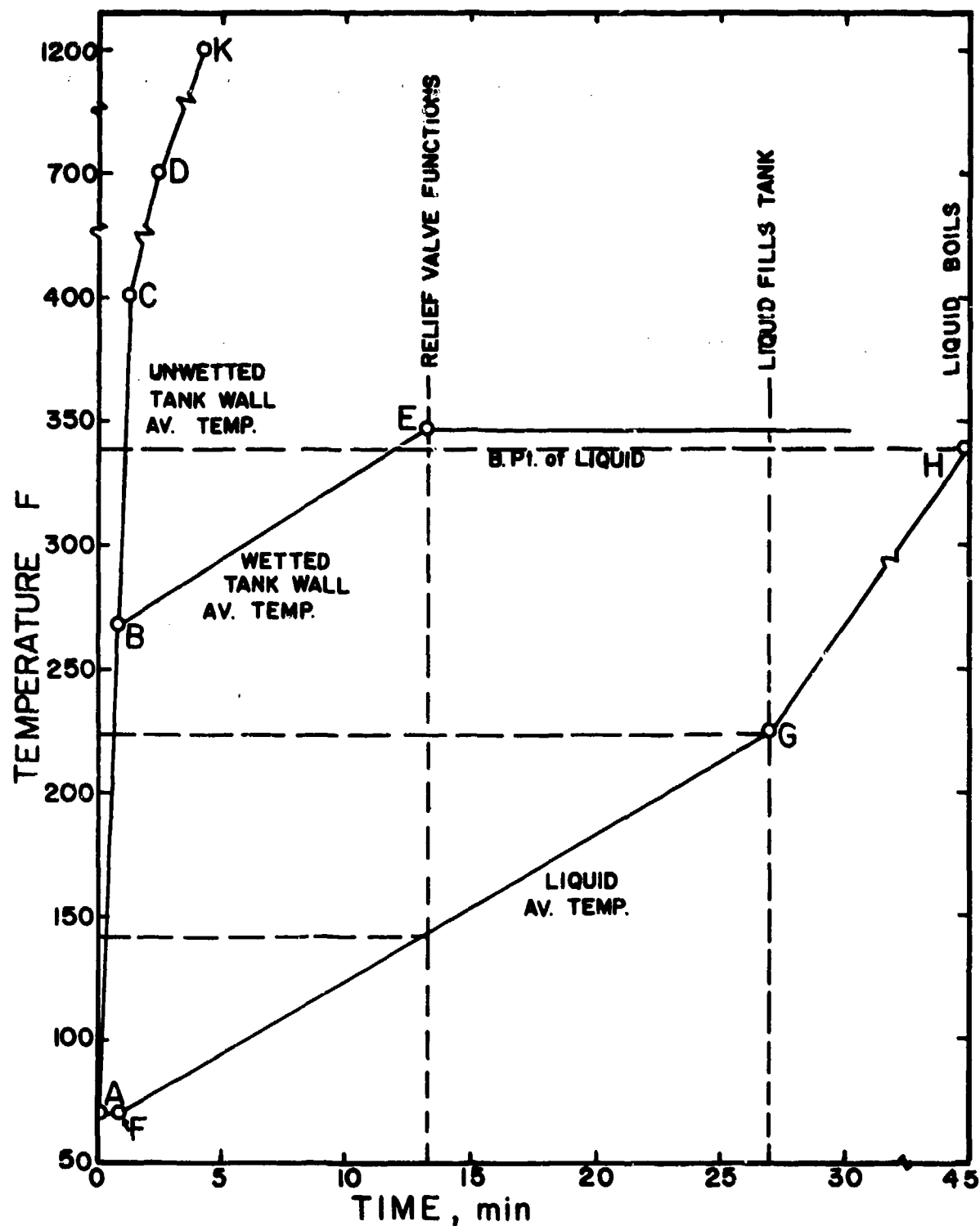
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Fig. 4 - Heating of bare tank

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assumed that the tank is filled at an ambient temperature of 68°F (20°C) and 1 atmosphere pressure with an ullage of 5%. Other pertinent assumptions and calculations are given in Appendix II, Part II.

At point A in Figure 4 an ambient temperature of 68°F (20.0°C) and zero time marks the start of the heating of the tank wall. For a period of about 0.72 minutes the tank wall heats to an average temperature of 266°F, shown as line AB, while there is essentially no heating of the $H_2O_2$ solution, shown as line AF. The line BC shows the continued rapid heating of that portion of the wall not wetted by the $H_2O_2$ solution resulting from the ullage. In 1.2 minutes the wall reaches an estimated 400°F, in 2.4 minutes 700°F, and 4.2 minutes 1200°F, the approximate melting point of aluminum. Thus we predict that the tank will fail in less than 5 minutes in such an intense, enveloping fire as is stipulated.

If, however, some mechanism not envisioned can cool the unwetted wall of the tank and it does not fail, then a continued sequence of events is as follows:

(a). $\theta$ = 0.72 min.
   When the wetted portion of the inside tank wall reaches a temperature corresponding to the normal boiling point of the $H_2O_2$ solution (258°F at $\theta$ = 0.72 min.), either nucleate boiling (17) or a decomposition heat-transfer mechanism (15) begins. In either case, the capacity to transfer heat to the liquid greatly exceeds the incoming heat flux and the liquid is heated, as line FG shows.

(b). $\theta$ = 0.72 to 13.2 min
   As the $H_2O_2$ liquid heats along line FG, it expands (more rapidly than the tank) and the ullage decreases thus compressing the gas and increasing the pressure in the tank. We estimate that the tank pressure reaches 53.7 psia (relief pressure) when the average liquid temperature reaches 142°F. As the tank pressure increases, the saturation temperature of the $H_2O_2$ solution increases and the wetted-wall temperature adjusts upward to give the required heat flux from the wall to the liquid, line BE. Then

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at θ = 13.2 minutes, the wetted-wall temperature
reaches 350°F and, as shown by the vertical dashed
line in the Figure, the relief valve functions.
However, vapor still remains in the tank at this
time.

(c). θ = 13.2 to 26.9 min
When the tank pressure reaches 53.7 psia, the average
wetted-wall temperature remains at about 246°F as
the $H_2O_2$ reaches 223°F, and the expanding liquid
fills the tank, point G. $H_2O_2$ liquid vents, adding
to the fire.

(d). θ = 26.9 to 44.8 min
The $H_2O_2$ continues to heat until its saturation
temperature at 53.7 psia is reached (point H).
Explosive vapor then forms (explosive limit at 53.7
psia = 18.5 mole percent (16)) in a tank above its
ignition temperature (302°F for inert materials such
as aluminum (3)).

Insulated Tank - In a fire situation, insulated
tanks have a decided advantage over bare tanks. This
advantage derives from the opacity of the insulation to
radiation; thus heat transmits through the insulation
only by conduction. As shown in Figure 5, insulation
reduces the heating rate of the tank wall. With the 2.76-
inch insulation, the average tank-wall temperature is
estimated at 30 minutes as only 144°F assuming no heat
loss to the liquid (line AC in Figure 5). For 1 inch
insulation, it reaches an average of 266°F in 29.1 minutes
to give an inside-wall temperature of 258°F, the normal
boiling point of the $H_2O_2$ (see line AB). Alternately,
if we assume that all of the heat transferred is dumped
into the $H_2O_2$ solution, the temperature rise would be
2°F for the thick insulation and 4°F for the one inch
insulation (line AD).

Such insulations as glass wool, 85% magnesia and
rock wool exhibit thermal conductivity of about
.043 $\frac{Btu}{(hr) x (ft) (°F)}$), however the recommended maximum
temperature for their use is only 500°F (18). In hydro-
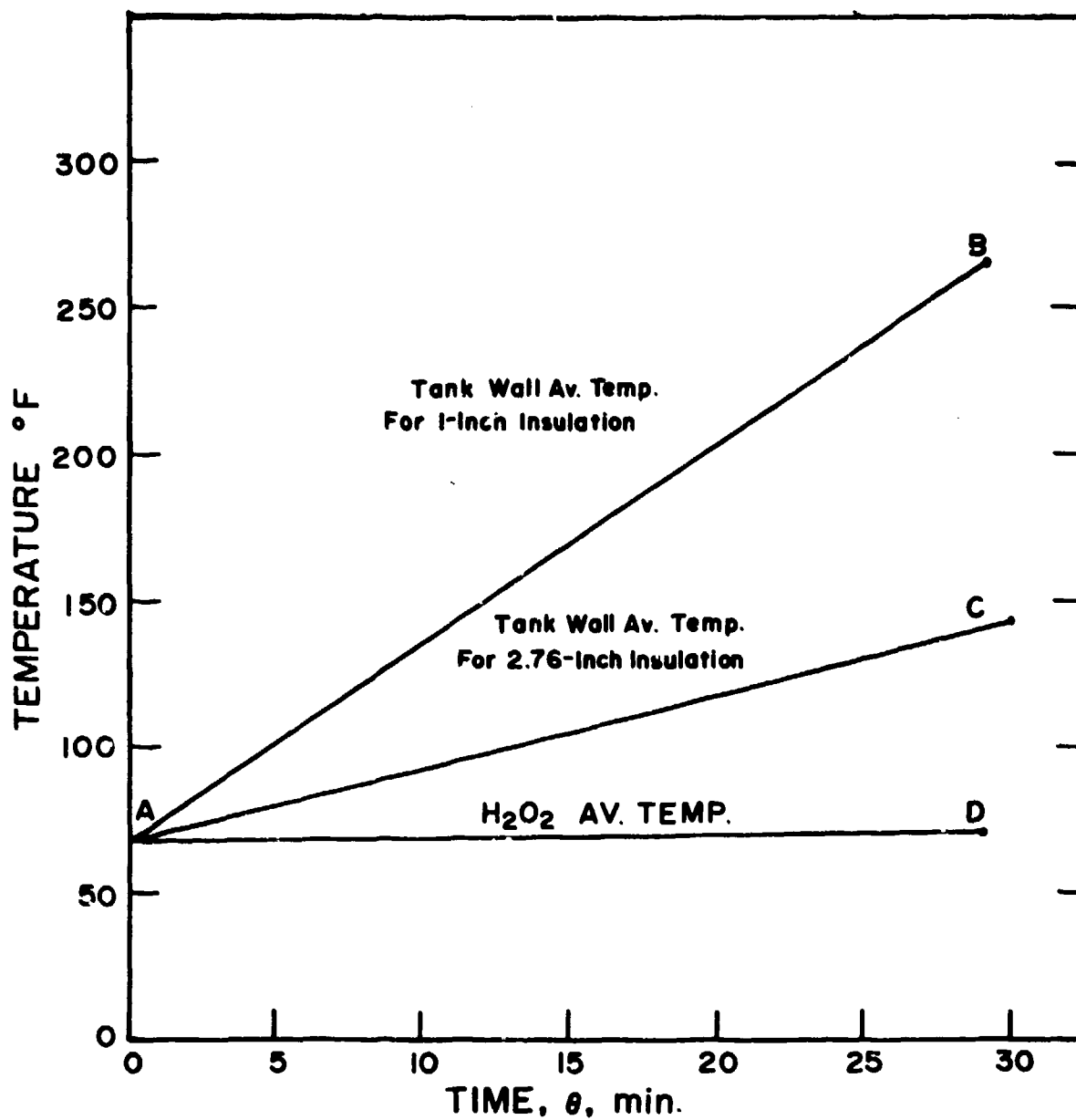carbon fires, average environmental temperatures of

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Fig. 5 – Temperature increase for insulated tanks

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about 1700°F are estimated (12).

## DISCUSSION

The data in Figure 3 show that 70 percent $H_2O_2$ solution free of impurities (Curve A) releases heat at a level which would allow ready dissipation even with insulation on the 4,000 gallon tank. For the convection only cooling mode (the conservative case) this Figure predicts that the $H_2O_2$ in a bare aluminum tank could reach a temperature of 257°F (125°C) before self heating occurs. The self-heating temperatures for the one-inch and 2.76-inch thick insulation cases are 222°F (106°C) and 197°F (92°C) respectively.

Should the $H_2O_2$ be contaminated so that the decomposition rate were five times (Curve B) that observed in our laboratory experiments, these self-heating temperatures would be somewhat lower. Thus, the critical temperature for the bare tank becomes 208°F (98°C), that for the tank with one inch of insulation becomes 170°F (77°C), and that for the tank with 2.76 inches of insulation becomes 142°F (61°C).

All of these temperatures are above ambient conditions found even in the tropics and hence should not rule out the use of insulation for containers of this size. This evaluation is valid if the peroxide is free from contaminants. The effect of higher decomposition rates on the self-heating temperature can be estimated by raising Curve A by the proper amount.

Insulated tanks demonstrate a distinct advantage over the bare tanks during exposure to an intense fire. The analysis illustrated in Figure 4 delineated several regimes of hazard for the bare tank. The first of these is early in the fire when we predict the unwetted wall of the tank would become very hot. Tests on 250 gallon steel LPG tanks by the Railroad Tank Car Safety Research and Test Project (12) found that the unwetted wall in an intense fuel fire reached 550°F (288°C) in two minutes and 800°F (427°C) in 4 minutes. Such temperatures, which support our analysis, would lead to rupture of the aluminum tank before the liquid phase absorbed sufficient

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heat to expand and fill the ullage. Although the wetted
wall can be kept at a modest temperature by nucleate
boiling, no physical mechanisms can afford adequate
cooling for the unwetted wall.

A second hazard regime occurs when the liquid fills
the tank and liquid oxidizer is added to the fire. This
will intensify the fire (raise the flame temperature).
Since various $H_2O_2$-organic mixtures detonate (3), such
an event also cannot be ruled out at this stage.

The third hazard regime comes after some liquid has
boiled off and been vented. Vapor again occupies a
portion of the tank and vapor will vent. However, the
concentration of the $H_2O_2$ in the vapor phase will exceed
18.8%, the lower limit for vapor phase explosion at the
design relief pressure, 53.7 psia.

All of these hazardous regimes are avoided by adding
insulation to reduce heat transfer from the fire to the
tank and contents. Even though the wall temperature for
the one inch insulated tank would reach the $H_2O_2$ boiling
point in 30 minutes, termination of the fire at this
time would preclude a significant rise in liquid tem-
perature (4°F for 1 inch insulation). The margin between
the liquid temperature and the self-heating temperature
would be large for stabilized peroxide.

The advantage afforded by insulation during the fire
situation considerably exceeds the disadvantage associated
with insulation during normal storage. During a fire,
the insulation comprises the major thermal resistance
between the fire and the tank since radiation (about 90%
of total) is the major mode of heat transfer. Thus, the
low thermal conductivity of the insulation is controlling
during a fire and the 2.76 inch insulation reduces the
amount of heat transferred to about one percent that
expected for the uninsulated tanks.

During normal storage, convection is the major heat
transfer mode to dissipate heat from the tank. The
exterior free convection film constitutes the major
thermal resistance for transfer from the bare container
and is a significant portion of the resistance for the

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insulated tank. Thus, the insulation does not have the overriding control of heat transfer for normal storage that it does for the fire environment.

The decomposition of stabilized $H_2O_2$, even at elevated temperatures, contributes much less heat than that derived from an external fire and this heat source has been disregarded in the heat transfer analysis.

Gas formation from peroxide decomposition will be slight. For example, the 4,000 gallon tank decomposing at the rate found in our studies would yield only 250 $ft^3$/ hr at the normal boiling point of 257°F (125°C). The vent requirement for the period "initial relief to shell full" is likewise low, 60 $ft^3$/hr. The liquid vent requirement for the shell full regime would be 120 $ft^3$/hr. If the tank should survive beyond the shell full stage and the heat from the fire was going into $H_2O_2$ vaporization, a vent capacity of $2.5-3.0 \times 10^5$ $ft^3$/hr. would be necessary.

The concentration of the peroxide carried in a container can affect the degree of hazard. One aspect of the hazard is explosion of the vapor phase. Explosion requires a minimum hydrogen peroxide concentration in the vapor phase and thus depends on the temperature and concentration of the liquid phase generating the vapor. At one atmosphere pressure, 26 mole % and above will explode if initiated by a spark or a catalyst (3). Ninety wt—% $H_2O_2$ liquid forms a vapor with 26 mole % $H_2O_2$ at 243°F whereas 74 wt % $H_2O_2$ must be heated to its boiling point, 263°F, to attain this vapor concentration. Liquids with less than 74 wt. % $H_2O_2$ cannot reach the vapor explosion limit at one atmosphere pressure.

A change in system pressure alters the vapor explosion limit - increasing to 40 mole % $H_2O_2$ at a lower pressure of 0.1 atmosphere (3) and decreasing to 18.5 mole % $H_2O_2$ at 53.7 psia, the pressure of interest for this study (16). A 64 wt. % liquid $H_2O_2$ can attain a vapor concentration of 18.5 mole % $H_2O_2$ under equilibrium boiling conditions at this higher pressure. Thus peroxide at a lower concentration would have less hazard potential. A reduction in the tank relief pressure would add another

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safeguard with respect to vapor explosions. By keeping
below the critical vapor concentration, the hazard of a
$H_2O_2$ vapor explosion toward the end of the fire would be
eliminated.

A lower peroxide concentration offers another safety
advantage. The adiabatic decomposition temperature for
70 wt. % is 450°F. Peroxides with concentrations between
11.3 and 64.7 wt. % have a much lower adiabatic decom-
position temperature, 212°F. The $H_2O_2$ heat of decomposi-
tion is not sufficient to evaporate all of the water in
the product plus that formed from decomposition unless
the concentration exceeds 64.7 wt. %. This factor would
be particularly advantageous if the product spilled onto
an active catalyst and rapid decomposition occurred.

Several minor factors affecting heat transfer have
not been considered in these calculations. Examples of
these factors are (1) the thermal resistance of the
oxide film on the aluminum container, (2) the thermal
resistance of air gap between the tank and the insulation,
and (3) the short time required for the outside wall to
reach steady-state conditions during a fire exposure.

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# RECOMMENDATIONS

1. Install insulation adequate to at least 1700°F on the 4,000 gallon aluminum shipping container. A one inch thickness with a thermal conductivity of 0.043 Btu/(hr)(ft)(°F) is appropriate. An equivalent combination of thickness and thermal conductivity could be substituted.

2. If full tank insulation is impractical, the unwetted portion of the tank should be covered with insulation.

3. Install a thermocouple to monitor the temperature of the tank contents.

4. Calculations be made to determine critical temperature rise rates to alert handlers to institute appropriate action.

5. Limit transport with aluminum containers to stabilized product with a concentration of 65% or less. This limitation would reduce the possibility of attaining the explosive vapor condition and would also limit the adiabatic decomposition temperature to 212°F (100°C) at one atmosphere pressure.

6. Reduce the pressure relief valve setting from 39 psig to 10 psig.

7. Examine the behavior of the tank cradle in an intense fire.

# APPENDIX I

## TANK DIMENSIONS
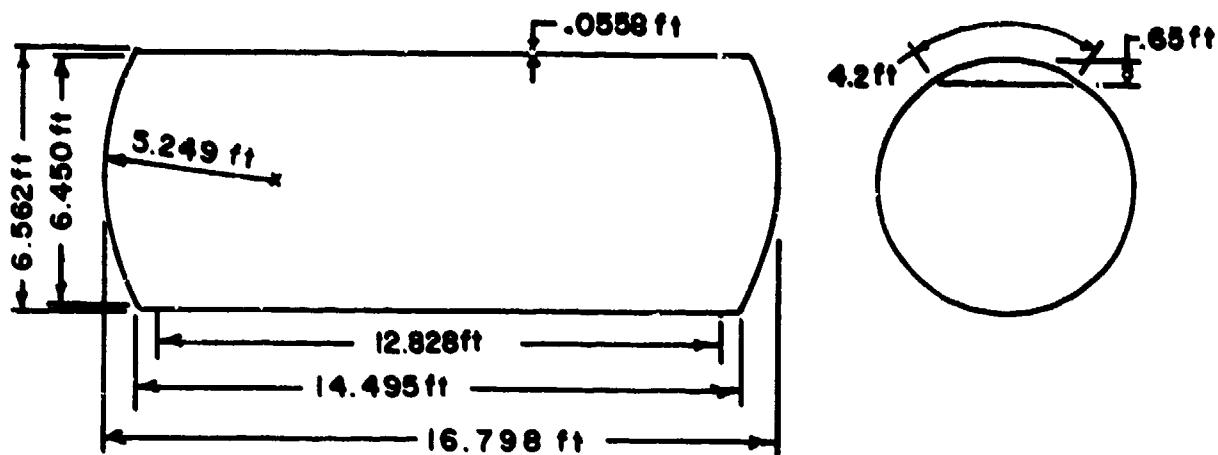


TANK VOLUME at 68°F = 490.4 cu ft = 3668 Gallons

INTERNAL SURFACE AREA at 68°F = 329.6 sq ft

EXTERNAL SURFACE AREA at 68°F = 335.3 sq ft

UNWETTED SURFACE AREA at 68°F = 60.4 sq ft

WETTED SURFACE AREA at 68°F = 269.2 sq ft

## APPENDIX II - CALCULATIONS

### Part I:   SELF-HEATING OF TANK

In this section, we give the basis for the heating and cooling curves of Figure 3.

### A.   Heating Curves

For curve A, we use a decomposition rate of 0.9% per year at 77°F (25°C) as based on NRL measurements shown in Figure 2.  If the heat of decomposition of 100% $H_2O_2$, $H_D$, is 1230 $\frac{Btu}{lb}$ , an average of the values given by

Schumb, et al (3) and Shanley (4), the heat released by decomposition of 70 weight percent $H_2O_2$ aqueous solution, $q_D$, is

$$q_D = \frac{(0.70)(M)(P_t)(H_D)}{24 \times 100} \text{ Btu/hr}$$

where

M = weight of $H_2O_2$ solution in the tank filled at 68°F (20°C) with a 5% ullage, and is (490.4 cu.ft.) x (.95) x (80.4 $\frac{lbs}{cu.ft.}$ ) = 37,460 lbs.

$P_t$ = peroxide decomposition rates in percent per day for various $H_2O_2$ temperatures as given in Fig. 2.

Values of $q_D$ as a function of the average bulk $H_2O_2$ temperature for curve A are presented in Table 3.

Curve B in Fig. 2 is arbitrarily chosen as 5 times the decomposition rate of curve A.

### B.   Cooling Curves

1.   Bare Tank (Curves 1 and 2 of Fig. 3) - For the bare tank, there are three resistances to the flow of heat from the liquid to the tank surroundings, which we can describe as $R_A$, $R_B$, and $R_C$.  $R_A$ is the thermal resistance to heat flowing between the liquid and the tank wall, $R_B$

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## TABLE 3

Heat Generated from 70 wt. % $H_2O_2$ with a Decomposition
Rate of 0.9% per Year at 25°C

| Temp. °C | Temp. °F | Decomp. Rate % per day | Decomp. Rate per hr. | Heat Released Btu/hr. |
|---|---|---|---|---|
| 25 | 77 | .0024 | $1.0 \times 10^{-6}$ | 32.3 |
| 30 | 86 | .0035 | $1.46 \times 10^{-6}$ | 47.1 |
| 35 | 95 | .0050 | $2.08 \times 10^{-6}$ | 67.1 |
| 40 | 104 | .0073 | $3.04 \times 10^{-6}$ | 98.0 |
| 45 | 113 | .0104 | $4.33 \times 10^{-6}$ | 140 |
| 50 | 122 | .0150 | $6.25 \times 10^{-6}$ | 202 |
| 55 | 131 | .0217 | $9.04 \times 10^{-6}$ | 292 |
| 60 | 140 | .0313 | $13.0 \times 10^{-6}$ | 419 |
| 70 | 158 | .0650 | $27.1 \times 10^{-6}$ | 874 |
| 80 | 176 | .135 | $56.3 \times 10^{-6}$ | 1820 |

is the resistance through the tank wall, and $R_C$ is the resistance between the tank and its surroundings. When we evaluate these resistances, we find that RC is enough larger than $R_A$ and $R_B$ that the latter two can be ignored in determination of the cooling curves. We proceed to justify this assumption.

The resistance to heat flowing from the liquid $H_2O_2$ to the tank wall, $R_A$, is the most difficult to estimate. According to Ostrach (19), study of heat transfer by natural convection in enclosures has attracted far less attention than that from the outside of vessels to their surrounding fluids. He attributes this fact to the added complication that in enclosures the boundary layer encloses a core region and the two are closely coupled. In lieu of correlations for horizontal cylinders we resort to the closest available model which has received analytical study. We estimate $R_A$ for the cylindrical tank by using the data for a square cross section, according to Newell and Schmidt (20) as Ostrach describes. We do this by equating the tank diameter to one side of the square. In the Newell-Schmidt correlation, the Nusselt number, $Nu_d$, is expressed as a function of the Grashof number, $Gr_d$, as follows:

$$\overline{Nu}_d = 0.0547 \ (Gr_d)^{\ 0.397}$$

where*

$$\overline{Nu}_d = \overline{h}_d D_i / k_f$$

*NOTE: Physical properties of $H_2O_2$ are taken from references (3), (21) and (22). When property extensions are necessary, methods are applied as recommended by Reid and Sherwood (23) or by Hougen and Watson (24).

and

$$Gr_d = \frac{D_i^{\ 3} \ \rho_f^{\ 2} \ g \ \beta_f \ \Delta t_{b-i}}{\mu_f^{\ 2}}$$

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Hence, $\bar{h}_D = 83.9 \dfrac{Btu}{(hr)(ft^2)(°F)}$ . Since the film resistance is the reciprocol of its conductance, the film resistance times the outside area becomes

$$A_o R_A = \frac{A_O}{(\bar{h}_D)(A_i)} \approx \frac{D_O}{(\bar{h}_D)(D_i)}$$

$$= \frac{6.562}{(83.9 \dfrac{Btu}{(hr)(ft^2)(°F)})6.45 \text{ ft}}$$

$$= 0.012 \frac{(hr)(ft^2)(°F)}{Btu}$$

The resistance to the flow of heat through the tank wall, $R_B$, depends on properties and condition of the aluminum wall. If we do not account for any oxide film, then $R_B$ times outside area is

$$A_o R_B = \frac{x_w D_O}{k_{av} D_{av}} = 4.8 \times 10^{-4} \frac{(hr)(ft^2)(°F)}{Btu}$$

for

$$t_{av} = 1/2 \ (88 + 78) = 83°F$$

To estimate $R_C$, the thermal resistance to heat flow from the tank wall to the surroundings, we consider heat energy transferral both by free convection and by radiation. These two mechanisms operate in parallel, so that

$$A_o R_C = \frac{A_O}{(\bar{h}_c + \bar{h}_r)\ A_o}$$

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According to Kreith (17), if the Rayleigh number ranges from $10^9$ to $10^{12}$ - for our case, the range is $10^9$ to $10^{10}$ - we may estimate $\overline{h}_c$ for air by

$$\overline{h}_c = 0.18 \, \Delta t_{o-a}^{1/3}$$

Values of $\overline{h}_c$ so obtained are given in Table 4.

The coefficient for radiation, $\overline{h}_r$ is determined in two steps. First, heat energy lost by radiation from the tank is estimated by the equation (25),

$$q_{rad} = \epsilon_1 \, \sigma \, (T_o^4 - T_a^4) \, A_{ww}.$$

Then, with values for the radiation energy interchange, values of $\overline{h}_r$ are determined by

$$\overline{h}_r = \frac{q_{rad}}{A_{ww}(t_o - t_a)}$$

Values of $\overline{h}_r$ are given in Table 4 as are those for $\overline{h}$, the sum of $\overline{h}_c + \overline{h}_r$, from which values of $A_c R_c$ are calculated to range from 1.7 to 0.7 (hr)(ft$^2$)(°F)/Btu.

Thus, $R_c$ is greater than $R_a$ by two orders of magnitude and greater than $R_B$ by three, and heat lost from the bare tank is

$$q_1 = \overline{h} \, A_{ww} \, \Delta t_{o-a}$$

Values of $q_1$ for various assumed outside wall temperatures are presented in Table 4 and are plotted as curve 1 in Figure 3. Notice that since we have assumed no resistance to heat flow from the liquid film or across the tank wall, $R_A$ or $R_B$, the $H_2O_2$ average temperature and the outside wall temperature become the same, and this applies in Figure 3. For heat lost by radiation, we assume the tank as a gray body radiating to its surroundings as a black body at 78°F, such conditions as exist on deck or in a large enclosure.

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TABLE 4 - Heat Lost from Bare Tank

| $t_o$ (°F) | $\Delta t_{o-a}$ (°F) | $\bar{h}_c$ | $\dfrac{q_1}{A_o} 10^{-2}$ | $\bar{h}_r$ | $\bar{h}$ | $A_o R_c$ | $A_o R_c^*$ | $q_1$ | $q_1^*$ |
|---|---|---|---|---|---|---|---|---|---|
| 87 | 9 | .37 | 1.97 | .22 | .59 | 1.69 | 2.70 | 1450 | 913 |
| 96 | 18 | .47 | 4.03 | .22 | .69 | 1.45 | 2.13 | 3400 | 2320 |
| 105 | 27 | .54 | 6.20 | .23 | .77 | 1.30 | 1.85 | 5700 | 4000 |
| 114 | 36 | .59 | 8.47 | .24 | .83 | 1.20 | 1.69 | 8190 | 5840 |
| 123 | 45 | .64 | 10.9 | .24 | .88 | 1.14 | 1.56 | 10900 | 7900 |
| 132 | 54 | .68 | 13.4 | .25 | .93 | 1.08 | 1.47 | 13800 | 10100 |
| 141 | 63 | .72 | 16.0 | .25 | .97 | 1.03 | 1.39 | 16700 | 12400 |
| 150 | 72 | .75 | 18.7 | .26 | 1.01 | .99 | 1.33 | 19900 | 14800 |
| 159 | 81 | .78 | 21.6 | .27 | 1.05 | .95 | 1.28 | 23300 | 17300 |
| 168 | 90 | .81 | 24.5 | .27 | 1.08 | .93 | 1.23 | 26600 | 20000 |
| 177 | 99 | .83 | 27.3 | .28 | 1.11 | .90 | 1.20 | 30100 | 22600 |
| 186 | 108 | .86 | 30.9 | .29 | 1.15 | .87 | 1.16 | 34000 | 25500 |
| 220 | 142 | .94 | 44.5 | .31 | 1.25 | .80 | 1.06 | 48600 | 26700 |
| 240 | 162 | .98 | 53.5 | .33 | 1.31 | .76 | 1.02 | 58100 | 43500 |
| 260 | 182 | 1.02 | 63.3 | .35 | 1.37 | .73 | .98 | 68300 | 50900 |
| 280 | 202 | 1.06 | 73.9 | .37 | 1.43 | .70 | .94 | 79100 | 58700 |
| 300 | 222 | 1.09 | 85.4 | .38 | 1.47 | .68 | .92 | 89400 | 66300 |

However, for curve 2, we assume that no heat is lost by radiation and that it is lost only by free convection, $q*_1$, as shown in Table 4.

When a thermal insulation is added to the outside of the tank, it has a resistance, $R_I$, of the same order of magnitude as exists from its outer surface to the air, $h_c$. However, as for the bare tank, $R_A$ and $R_B$ may be ignored. Then the total resistance to heat flow from the $H_2O_2$ is

$$R_T = \frac{1}{(\bar{h}_c + \bar{h}_r) A_I} + \frac{x_I}{k_I A_a}$$

The total heat lost from the insulated tanks, $q_1$, based on the outside area $A_I$ of the insulation is

$$q_1 = \frac{\Delta t_{,)-a}}{R_T}$$

Values are given in Table 5 for the 1-inch insulation both with and without radiation losses included, where $A_I = 281$ ft$^2$. The Table also gives the same information for the 2.76-inch insulation.

## Part II: FIRE INVOLVEMENT

As is evident in Figures 4 and 5, the presence of insulation on the tank affords protection in fire situations. Insulated tanks with either 2.76 or 1.0 inches of suitable insulation are protected for 30 minutes and more in an intense fire, yet failure of a bare tank is predicted in less than 5 minutes. In the estimations that follow, we assume the heat flux in the fire is 34,500 Btu/(hr)(ft$^2$) to the bare tank regardless of direction.

## A. Bare Tank

1. Tank walls heat with negligible heat of $H_2O_2$ – In the first heating phase, designated as line AB in Figure 1, the tank walls rise in temperature from 68 to an average of 266°F. The temperature drop across the

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TABLE 5 - Heat Lost from Insulated Tank

| $t_b$ (°F) | $\Delta t_{o-a}$ (°F) | $\Delta t_{I-a}$ | $\bar{h}_c$ | $\dfrac{q_{rad}}{A}$ | $\bar{h}_r$ | $AR_T$ (Rad.) | $AR_T$ (No Rad.) | $q_1$ (Rad.) | $q_1$ (No Rad.) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 1-inch Insulation* | | | | | |
| 87 | 9 | 4 | .29 | 3.66 | .92 | 2.79 | 5.41 | 906 | 467 |
| 105 | 27 | 11 | .40 | 10.3 | .93 | 2.71 | 4.46 | 2800 | 1700 |
| 123 | 45 | 20 | .49 | 19.1 | .96 | 2.65 | 4.00 | 4800 | 3160 |
| 141 | 63 | 28 | .55 | 27.4 | .98 | 2.61 | 3.78 | 6800 | 4680 |
| 159 | 81 | 36 | .59 | 36.0 | 1.00 | 2.59 | 3.65 | 8800 | 6240 |
| 177 | 99 | 44 | .64 | 45.0 | 1.02 | 2.56 | 3.52 | 10900 | 7900 |
| 220 | 142 | 62 | .71 | 66.6 | 1.07 | 2.52 | 3.37 | 15800 | 11800 |
| 240 | 162 | 71 | .75 | 78.2 | 1.10 | 2.50 | 3.29 | 18000 | 13800 |
| 260 | 182 | 80 | .78 | 90.2 | 1.13 | 2.48 | 3.24 | | 15800 |
| | | | | 2.76-inch Insulation** | | | | | |
| 87 | 9 | 1 | - | .91 | .91 | 6.63 | - | 398 | - |
| 105 | 27 | 3 | .26 | 2.74 | .91 | 6.38 | 9.37 | 1240 | 844 |
| 123 | 45 | 4.5 | .30 | 4.12 | .92 | 6.35 | 8.86 | 2080 | 1490 |
| 141 | 63 | 6 | .33 | 5.52 | .92 | 6.33 | 8.56 | 2920 | 2160 |
| 159 | 81 | 8 | .36 | 7.40 | .93 | 6.31 | 8.31 | 3760 | 2860 |
| 177 | 99 | 10 | .39 | 9.30 | .93 | 6.31 | 8.09 | 4600 | 3590 |
| 220 | 142 | 14 | .43 | 13.2 | .94 | 6.26 | 7.86 | 6650 | 5290 |
| 240 | 162 | 16 | .45 | 15.1 | .95 | 6.24 | 7.75 | 7610 | 6120 |
| 260 | 182 | 18 | .47 | 17.1 | .95 | 6.23 | 7.66 | 8560 | 6960 |

\* $AR_I = 1.96 \dfrac{(hr)(ft^2)(°F)}{Btu}$

\*\* $AR_I = 5.53 \dfrac{(hr)(ft^2)(°F)}{Btu}$

tank wall is

$$\Delta t_{i-o} = \frac{(34,500 \ \frac{Btu}{(hr)(ft)^2}) \ (0.0558 \ ft)}{(118.5 \ \frac{Btu}{(hr)(ft)(°F)}) \ (1 \ ft^2)} = 16°F$$

and at point B the inside wall temperature is 258°F, the saturation temperature of 70 wt % $H_2O_2$ at 1 atmosphere (14.7 psia) pressure.

During this period of some 0.72 minute, essentially all of the heat transferred from the fire heats the tank wall. This is because the resistance to the flow of heat from the tank wall to the liquid exceeds that of the flow from the fire to the bare wall by about an order of magnitude. The average wall resistance, $R_B$, as based on the outside area of the tank is

$$A_o R_B = \frac{x_w \ A_o}{k_w \ A_{av}} \approx \frac{x_w \ D_o}{k_w \ D_{av}} = \frac{(0.0558 \ ft) \ (6.562)}{(118.5 \ \frac{Btu}{(hr)(ft)(°F)}) \ (6.506)}$$

$$= 4.7 \times 10^{-4} \ \frac{(hr)(ft^2)(°F)}{Btu}$$

for a $t_w = 1/2(266 + 68) = 167°F$.

When we assume free convection of an enclosure according to Ostrach (19) as before for a square cross section and use a maximum temperature difference between the wall and fluid to give a minimum thermal resistance for the liquid, the heat conductance from the wall to the liquid, $h_D$, is

$$\bar{h}_D = (\frac{k_f}{D_i}) \ (0.054) \ \left( \frac{D_i^3 \rho_t^2 \ g \ \beta_f \ \Delta t_{i-b}}{\mu_f^2} \right)^{0.397}$$

Using $\Delta t_{i-b} = 258-68 = 190°F$, $\bar{h}_D$ becomes $267\frac{Btu}{(hr)(ft^2)(°F)}$

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and the thermal resistance from the wall to the $H_2O_2$ is

$$A_o R_A = \frac{A_o}{\overline{h}_D A_i} = \frac{6.562}{(267)(6.450)} = 0.0038 \ \frac{(hr)(ft^2)(°F)}{Btu}$$

Thus, $\frac{R_A}{R_B} = \frac{0.0038}{4.7 \times 10^{-4}} = 8$, about 1 order of magnitude.

Then, accordingly, the heat required to raise one square foot of aluminum wall from 68° to 266°F with no heat loss is

$$Q = C_{p_{av}} \ \Delta t_{inc} \ W_{av}$$

For a $t_{av} = 1/2(266 + 68) = 167°F$, we find

$Q = (9.419)(0.2212)(198) = 412.5$ Btu.

Since the incoming heat energy is $34,500 \ \frac{Btu}{(hr)(ft^2)}$ , the time for it to pass to the wall is

$$\theta = \frac{Q}{q/A} = \frac{412.5 \ Btu}{34,500 \ \frac{Btu}{hr}} = 0.012 \ hrs = 0.72 \ min$$

2. Failure of tank wall in ullage space - Since there is an ullage of 5% when the tank is filled, assumed at 68°F (20°C) and 1 atm. pressure, about 60.4 $ft^2$ of the tank wall is not wetted. As a result, the incoming heat energy from the fire to this section of wall is transferred away at only a fraction of its incoming rate. For example, the maximum heat transferred down the wall from the unwetted to the wetted section is at a maximum temperature difference. If we assume this difference as 400-266 = 134°F for a length of 6 inches, the heat transferred down the wall, $q_k$ becomes

$$q_k = \frac{k_w \, A \Delta t}{\Delta X} = \frac{(125 \ \frac{Btu}{hr \ ft \ °F}) \ (.0558 \ ft) \ (1 \ ft) \ (134°F)}{(0.5 \ ft)}$$

$$= 1900 \ \frac{Btu}{hr}$$

for a width of 1 ft. This loss amounts to about 5% of the incoming energy. Further, if we assume black-body conditions, the maximum energy radiated from the unwetted surface is

$$\frac{q_{rad}}{A} = \sigma \ (T_{uw}^4 - T_{H_2O_2}^4)F = 0.171 \ \left[ (8.6)^4 - (5.28)^4 \right]$$

$$= 800 \ \frac{Btu}{(hr)(ft^2)}$$

This is about 2.3% of the total incoming energy. Thus, we estimate that heat lost from the unwetted portion of the tank wall loses less than 10% of that added by the fire. So the unwetted wall rapidly increases in temperature. Thus, by disregarding losses, we determine the time needed to heat the unwetted tank wall from 68°F to 400°, 700°, and 1200°F:

$$\theta = \frac{\text{heat capacity of tank wall}}{\text{rate of incoming heat energy}} = \frac{Q}{q}$$

For one square foot of wall surface, the weight at 68°F is

$$W_{68} = \text{(area) (thickness) (density)}$$

$$= (1 \ ft^2) \ (.0558 \ ft) \ (168.8 \ \frac{lb}{ft3})$$

$$= 9.419 \ lbs.$$

As the tank wall temperature increases, it expands. This expansion is

$$L_t = L_{68} \ [1 + \alpha \ (t-68)(10^{-6})]$$

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at 400 and 700°F respectively,

$$L_{400} = L_{68} \ (1.0045) \ \text{and}$$

$$L_{700} = L_{68} \ (1.0066).$$

Further

$$W_{400} = \frac{W_{68}}{(L_{400})^3} = \frac{9.419 \ \text{lbs}}{(1.0045)^3} = 9.293 \ \text{lbs} \quad \text{and}$$

$$W_{700} = \frac{W_{68}}{(L_{700})^3} = \frac{9.419 \ \text{lbs}}{(1.0092)^3} = 9.164 \ \text{lbs}.$$

The heat energy to increase the wall temperature from 68 to t°F is $(W_{av}) \ (C_{p_{av}}) \ (\Delta t_{inc})$, and accordingly, for the range 68 to 400°F: $Q = 1/2(9.419 + 9.293) \ (.2266) \ (332) = 702$ Btu, and for 68 to 700°F: $Q = 1/2(9.419 + 9.164) \times (.2365) \times (632) = 1389$ Btu. Hence, the times required to heat the unwetted wall to specific temperatures are estimated as

$$\theta_{400} = \frac{(702 \ \text{Btu})(60 \ \frac{\text{min}}{\text{hr}})}{(34,500 \ \frac{\text{Btu}}{\text{hr}})} = 1.22 \ \text{min,}$$

$$\theta_{700} = \frac{(1389)(60)}{34,500} = 2.42 \ \text{min, and}$$

$$\theta_{1200} \cong 2.42 \ \frac{1200-68}{700-68} = 4.3 \ \text{min.}$$

In Figure 3, the lines BC, CD, and DK show these times and temperatures. The yield strength of 99.6 aluminum (28) decreases as its temperature increases:

| Temp.,°F | 75 | 300 | 400 | 500 | 600 | 700 |
|---|---|---|---|---|---|---|
| Yield strength,psi | 5000 | 3500 | 3000 | 2000 | 1500 | 1000 |
| Percent of 75°F | 100% | 70% | 60% | 40% | 30% | 20% |

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and the metal melts at c.a. 1195°F. Thus, we predict a failure by melting for the intense fire situation examined here.

   3.  Heating of the $H_2O_2$ solution - If "bumping" of the liquid, a smaller fire than assumed, or some other unenvisioned mechanism results in a nonfailure of the bare tank as we predict, then the 70 wt % $H_2O_2$ in the tank begins to heat as the wetted section of wall reaches about 258°F, the normal boiling point of the $H_2O_2$ solution (3). According to Rohsenow (29), nucleate boiling would begin at this approximate wall temperature. In addition, Sanborn, et al, (15) describe a decomposition heat-transfer mechanism which begins at a somewhat lower temperature for a 90% $H_2O_2$ aqueous solution. Either of these mechanisms would easily accommodate the incoming heat energy flux.

   Consider the ullage of the tank. For 68°F, Appendix I shows the ullage as 24.47 cu. ft. In a fire, this ullage first increases as the walls heat and the liquid does not. At point B of Fig. 4, the ullage becomes

$$(24.47 \text{ ft}^3) \; [1 + (13.3) \; (198) \; (10^{-6})]^3 = 24.66 \text{ ft}^3.$$

After point B, the liquid expands more rapidly than the wall, and the ullage decreases. Our interest is to determine if the ullage change creates a tank pressure of 53.7 psia, the pressure which actuates the relief valve system. To do this, we first estimate the volume change at Point B needed to produce the actuating pressure by the perfect gas law

$$V_{68} = 24.75 \text{ ft}^3 \; (\frac{14.7}{53.7}) = 6.78 \text{ ft}^3.$$

Now we correct this volume for increasing temperature again assuming the ideal gas law.

| Vapor Temp., °F | 68 | 176 | 237 | 338 |
|---|---|---|---|---|
| Ullage, ft$^3$ | 6.775 | 8.161 | 8.944 | 10.24 |

and choose the vapor temperature as 237°F by the estimate
that

$$t_{vapor} = 1/2 \left[ \frac{2}{3} (230-68)_{liquid} + 1/2(258 + 238)_{wall} \right]$$

$$= 237°F.$$

This prediction gives a 9.0 cu. ft. ullage, along with
a vapor temperature of 237°F and an average wall
temperature of 346°F. For these conditions the original
37,460 lbs of $H_2O_2$ has expanded to 479.9 cu. ft., a
density of $78.05 \frac{lb}{ft^3}$ , corresponding to a temperature
of 142°F. Thus, when the $H_2O_2$ solution average tempera-
ture reaches 142°F, the relief-system functions. The
time required for a $\Delta t$ of 74°F is

$$\theta = \frac{M C_{p_H} \Delta t \; 60}{A_{ww} (q/A)} = 12.7 \text{ min.}$$

Thus, the valve functions at about 12.7 + .72 = 13.4 min.

The estimated time for the liquid to fill the tank is

$$\frac{Q}{q} = \frac{W c_{p_H} \Delta t}{(q/A)(A_{wa})} \; (60) \; = 17.9 \text{ min}$$

where: $Q$ = heat energy to heat $H_2O_2$ to 223°F

$A_{wa}$ = av. wetted area - 1/2(284.6 + 330.9), $ft^2$

$\Delta t = 223 - 142 = 81°F.$

We obtain the temperature, 223°F, at which the tank goes
liquid full by considering the density of the 70 wt %
$H_2O_2$ solution. When the tank is filled its volume is

$$V_{68} \left[ 1 + \alpha (346-68) \right]^3 = 496 \; ft^3$$

where, $V_{68}$ = tank volume at 68°F, 490.4 cu ft.
The density of the $H_2O_2$ then is

$$\rho_f = \frac{M}{V_{346}} = \frac{37,460 \text{ lbs}}{496 \text{ ft}^3} = 75.5 \frac{\text{lb}}{\text{ft}^3}$$

and 70 wt % $H_2O_2$ has this density at 223°F.

The time to heat the liquid from 142° to 223°F is

$$\frac{Q}{q} = \frac{(37,460 \text{ lbs})(0.768 \frac{\text{Btu}}{(\text{lb})(°F)})(223-142)(60 \frac{\text{min}}{\text{hr}})}{(34,500 \frac{\text{Btu}}{\text{hr ft}^2})(307.8 \text{ ft}^2)}$$

$$= 13.7 \text{ min.}$$

Therefore, the total time is 13.2 + 13.7 = 26.9 min.

The liquid would reach its boiling point at 53.7 psia, if we disregard the overflow, in an additional 18 minutes producing explosive vapors.

$$\frac{(37,460 \text{ lbs})(0.791 \frac{\text{Btu}}{\text{lb°F}})(338°-223°F)(60)}{(34,500 \frac{\text{Btu}}{\text{hr ft}^2})(330.9 \text{ ft}^2)} = 17.9 \text{ min.}$$

## B. Insulated tank

Since insulation, we assume, is opaque to radiant energy, a heat flux of 34,500 Btu/(hr)(ft²) does not apply. To determine a heat flux, we consider the exposed insulation temperature as 1700°F, the estimated temperature of the fire environment (12). We assume further that the thermal resistance of the insulation is controlling. Then the heat flux to the tank is

$$\frac{q}{A_o} = \frac{\Delta t_I}{\frac{X_I \, A_o}{k_I \, A_a}}$$

For 1-inch insulation, the flux is 850 $\frac{Btu}{(hr)(ft^2)}$; while for 2.76-inch, it is 320 Btu/(hr)(ft$^2$).

With these fluxes, first assume the extreme that all of the incoming energy goes to heat the tank wall, and calculate the time to heat the wall from 78 to 266°F, the approximate condition for nucleate boiling or decomposition heat transfer mechanisms. These times are estimated by

$$\theta = \frac{W_{av}\ c_{P_{Al}}\ (266\text{-}78°F)}{q/A_o}$$

and are 28.2 minutes and 75 minutes for the 1.0- and the 2.76-inch insulation, respectively. For the thicker insulation, the wall temperature at 30 minutes is 153°F. These values are shown in Fig. 5 as points B and C, where B is for the 1-inch insulation.

Now consider the temperature rise of the $H_2O_2$ solution. In this case, assume that all the heat energy goes to the liquid. For the 37,460 pounds of $H_2O_2$ with an average specific heat of 0.745 Btu/(lb)(°F) and an area of 274 ft$^2$, a $H_2O_2$ temperature increase of 4°F for the 1-inch and 2°F for the 2.76-inch insulation is estimated.

With these temperatures for the wall and the liquid, the thermal resistance of free convection in the enclosure is estimated as before to give values much less than those for the insulation. Thus, the original assumption that the insulation controls the heat transfer from the fire to the tank and contents is satisfactory even for the extremes assumed.

## Part III: LIST OF SYMBOLS

A     - area, ft$^2$

$A_a$     - average area of insulation normal to heat flow

$A_{av}$ — average area of tank wall, $[1/2(A_i + A_o)]$

$A_I$ — outside area of tank insulation

$A_i$ — area, tank inside

$A_o$ — area, tank outside

$A_{ww}$ — outside area of tank less the area unwetted by the $H_2O_2$ solution; 335-61 = 274 ft$^2$ at 68°F

$C_{p_{Al}}$ — average heat capacity of aluminum over a temperature range $\dfrac{Btu}{(lb)(°F)}$

$C_{p_H}$ — average heat capacity of 70% $H_2O_2$ over a temperature range $\dfrac{Btu}{(lb)(°F)}$

$D_{av}$ — average diameter of tank, ft $[1/2 (D_i + D_o)]$

$D_i$ — inside diameter of tank, ft

$D_o$ — outside diameter of tank, ft

$F$ — view factor = 1, dimensionless

$Gr_d$ — Grashof number

$H_D$ — $H_2O_2$ heat of decomposition, Btu/lb

$L_t$ — length at specified temperature, ft

$M$ — weight of $H_2O_2$ in tank, lb

$\overline{Nu}_d$ — Nusselt number

$P_t$ — rate of $H_2O_2$ decomposition at specified bulk liquid temperature, %/day

$Q$ — quantity of heat, Btu

$R$ — thermal resistance to heat flow, $\dfrac{(hr)(°F)}{Btu}$

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$R_A$    - thermal resistance between liquid and tank wall

$R_B$    - thermal resistance through tank wall

$R_C$    - thermal resistance between tank and surroundings

$R_I$    - thermal resistance through insulation

$R_T$    - thermal resistance, total

$T$      - absolute temperature, °R

$T_a$    - air temperature, absolute = 460 + 78 = 538°R

$T_{H_2O_2}$ - $H_2O_2$ surface temperature, absolute

$T_o$    - outside wall temperature, absolute

$T_{uw}$   - inside temperature of unwetted tank wall, absolute

$W_t$    - weight of 1 $ft^2$ of aluminum wall at specified temperature; 9.419 lb    68°F

$W_{av}$   - average weight of 1 $ft^2$ of aluminum wall over a temperature range

$V$      - volume, $ft^3$

$g$      - acceleration of gravity, 32.2 $\dfrac{ft}{sec^2}$

$h$      - heat transfer coefficient $\dfrac{Btu}{(hr)(ft^2)(°F)}$

$\overline{h}$      - sum of $\overline{h}_c + \overline{h}_r$

$\overline{h}_c$    - average heat transfer coefficient for free convection

$\overline{h}_D$    - liquid film coefficient of heat transfer

$\overline{h}_r$    - heat transfer coefficient for radiation

$k_{av}$    - thermal conductivity of aluminum at $t_{av}$; 118.5 $\dfrac{Btu}{(hr)(ft)(°F)}$

$k_f$ - thermal conductivity of $H_2O_2$ at $t_f$;
0.346 $\dfrac{Btu}{(hr)(ft)(°F)}$

$k_I$ - insulation thermal conductivity; used value of
0.043 $\dfrac{Btu}{(hr)(ft)(°F)}$

$k_w$ - thermal conductivity of aluminum at $t_w$

$q/A$ - heat flux; 34,500 $\dfrac{Btu}{(hr)(ft)^2}$ for bare tank exposure
to fire

$q$ - heat transfer rate, Btu/hr

$q_D$ - rate of heat release by $H_2O_2$ decomposition, Btu/hr

$q_k$ - heat transfer rate along tank wall

$q_1$ - heat lost from tank, Btu/hr

$q_1^*$ - heat lost from tank by free convection

$q_{rad}$ - net radiation interchange of the tank with
surroundings, Btu/hr

$t$ - temperature, °F

$t_a$ - temperature of air

$t_{av}$ - average temperature of aluminum

$t_b$ - temperature of bulk $H_2O_2$

$t_F$ - temperature of liquid $H_2O_2$ film at tank wall,
$\dfrac{t_i + t_b}{2}$

$t_i$ - temperature of tank inside wall

$t_o$ - temperature of tank outside wall

$t_w$ - average tank wall temperature

$\Delta t$    - temperature difference or change, °F

$\Delta t_{b-i}$    - temperature difference, bulk liquid to inside wall

$\Delta t_{I-a}$    - temperature difference, outside of insulation to air

$\Delta t_I$    - temperature difference across insulation; used 1700-68 = 1632°F for fire exposure

$\Delta t_{inc}$    - temperature increase of tank wall

$\Delta t_{i-b}$    - temperature difference, inside wall to bulk $H_2O_2$

$\Delta t_{i-o}$    - temperature difference across tank wall

$\Delta t_{o-a}$    - temperature difference between outside tank wall and air, 78°F assumed for $t_a$

$X_I$    - insulation thickness, ft

$X_w$    - tank wall thickness, 0.0558 ft

Greek Symbols

$\alpha$    - coefficient of linear expansion for 99.6% Al (27), $13.6 \times 10^{-6}$ °F$^{-1}$

$\beta_f$    - coefficient of thermal expansion of fluid; values for water used (17), $1.6 \; 10^{-4}$ °F$^{-1}$

$\epsilon_1$    - emissivity, dimensionless; 0.2 used for heavily oxidized aluminum surface (26); 0.85 used for insulation

$\theta$    - time period, minutes

$\sigma$    - Stefan-Boltzman constant; $0.1714 \times 10^{-8}$ $\dfrac{Btu}{(hr)(ft^2)(°R)^4}$

$\rho_f$    - $H_2O_2$ density

$\mu_f$    - viscosity of $H_2O_2$ at $t_f$; $7.25 \times 10^{-4} \; \dfrac{lb}{(ft)(sec)}$ at 83°F

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